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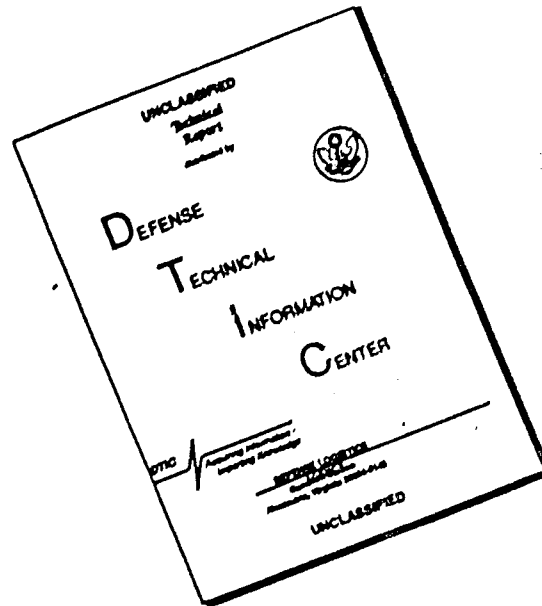


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THE UNIVERSITY OF WESTERN ONTARIO



DEPARTMENT OF PHYSICS  
MOLECULAR EXCITATION GROUP

TRANSITION PROBABILITIES OF MOLECULAR BAND SYSTEMS

XX: Tabulated Klein-Dunham Potential Energy Functions  
for Ten States of  $C_2(4)$ ,  $O_2(2)$ ,  $OH(2)$  and  $SiO(2)$

by

W. R. JARMAIN

JULY 1st, 1961

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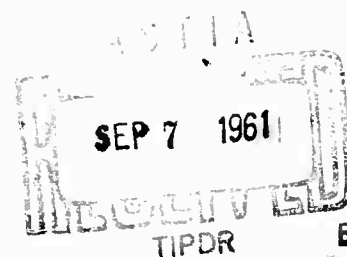
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# ABSTRACT

Sets of classical turning points, together with the corresponding vibrational energies, are given at an interval of one half a unit of quantum number for the following molecular states:  $C_2$ ,  $X^3\Pi_u$ ,  $A^3\Pi_g$ ,  $B^3\Pi_g$ ,  $c^1\Pi_g$ ;  $O_2$ ,  $X^3\Sigma_g^-$ ,  $B^3\Sigma_u^-$ ;  $OH$ ,  $X^2\Pi_i$ ,  $A^2\Sigma^+$ ;  $SiO$ ,  $X^1\Sigma^+$ ,  $A^1\Pi$ .

These numbers, representing points on potential curves, were derived from Klein's formulae by analytical differentiation, and numerical integration with a necessary analytic approximation over a small part of the range.

## 1. INTRODUCTION

An earlier Scientific Report (Jarmain 1960a) contained tables of classical turning points for fifteen diatomic molecular states, computed by a modified Klein-Dunham series method described in detail elsewhere (Jarmain 1960b). At higher levels of unfavourable states, however, these series may diverge, or converge so slowly that there are not enough terms formulated to produce sufficiently accurate results. It was not considered worthwhile to work out coefficients for further terms because they become algebraically unwieldy.

The procedure adopted was to perform necessary differentiations analytically, then to evaluate integrals numerically on an I.B.M. 650. This is an improved method of constructing potential energy functions up to a vibrational quantum number of thirty. The only important limitation remaining is that spectroscopic observations are not available for more than the lowest few levels of certain molecular states.

## 2. METHOD

For the minimum and maximum values,  $r_{1,2}$  of the internuclear distance for a molecule vibrating with an energy  $U$ , Klein (1932) gives the formula

$$(1) \quad r_{1,2}(U) = \left( \frac{f}{g} + r^2 \right)^{1/2} \pm f$$

with  $f$  and  $g$  defined in terms of the auxiliary function



$$(2) \quad S(U, \kappa) = \frac{1}{\pi(2\mu)^{1/2}} \int_0^{I'} [U - E(I, \kappa)]^{1/2} dI$$

Here,  $E(I, \kappa)$  is the sum of vibrational and rotational energies for any level up to  $U$ ; the action variable  $I = h(v + 1/2)$ ;  $\kappa = [J(J+1)h^2]/8\pi^2\mu$  with  $J$  the rotational quantum number;  $\mu$  is the reduced mass of the molecule;  $I = I'$  when  $E = U$ .

Then

$$(3) \quad f = \frac{\partial S}{\partial U} \Big|_{\kappa=0} \text{ and } g = - \frac{\partial S}{\partial \kappa} \Big|_{\kappa=0}$$

Replacing  $v + 1/2$  by  $V$  and differentiating under the integral sign,

$$(4) \quad \begin{aligned} f(U) &= \frac{1}{2\pi(2\mu)^{1/2}} \int_0^{V'} [U - E(V, \kappa)]^{-1/2} dV \\ g(U) &= \frac{h}{2\pi(2\mu)^{1/2}} \int_0^{V'} \frac{\partial E}{\partial \kappa} [U - E(V, \kappa)]^{-1/2} dV \end{aligned}$$

evaluated at  $\kappa = 0$  for the normal potential curve (no rotation).

As in previous work, the vibrational quantum number is not formally restricted to integral values. The integrals in (4) cannot however be calculated over the whole range 0 to  $V'$  by Simpson's or other method of numerical integration, because the integrands become infinite at the upper limit  $V'$ . This difficulty is circumvented by using a good approximation to  $[U - E]^{-1/2}$  near  $V = V'$ , as outlined below.

The program written for the I.B.M. 650 permits subdivision

of one unit in  $V$  for numerical integration according to the relation

$$\left(\frac{1}{H}\right) V_m \leq 519$$

where  $H$  is the size of a subdivision, that is  $\frac{1}{H}$  is the number of subdivisions per unit quantum number,  $V_m$  is the maximum  $V$  to be used, and the limit of 519 is dictated by computer storage space. Suppose for illustration that  $1/H$  is chosen to be 24 and  $V' = 3.5$ . Energies can be interpolated, if not already known, at the 85 points of division using arcs of two parabolae. Then Simpson's Rule can be applied to the first 82 subdivisions, leaving the  $f$ -integrand to be approximated in the remaining two subdivisions by an analytically integrable function.

The function chosen is of the form  $y = ax^{-p}$  with  $x = 0$  at  $V = V'$ , and passing through  $(H, y_1)$  and  $(2H, y_2)$ ,  $y_1$  and  $y_2$  being the second and third last ordinates respectively. These conditions determine 'a' and  $p$  (the latter is very near one half). The 'end contribution' to the integral is easily found to be  $2Hy_2/1-p$ , with  $1-p$  approximated closely by the polynomial  $2.6640 - 2.0403R + 0.36067 R^2$  (from a Taylor Series expansion of a logarithm), where  $R \equiv y_1/y_2$ .

Included also in the integrand for  $g(U)$  is  $\frac{\partial E}{\partial K}|_{K=0}$  which equals  $q B_v$  (Jarman 1960b) where  $q = 8\pi^2 \mu/h^2$ , a constant that can be combined with that in front of the integral. Three  $B_v$  values are known by interpolation for the 'end contribution' to  $g$ , but there is the question of how they should be weighted when the area is found analytically. If a parabola  $y = Ax^2 + Bx + C$  is passed through these

final three 'points' of a set of  $B_v$ , its coefficients can be evaluated and the product of the parabolic function with  $y = ax^{-p}$  integrated. The weighting factors turn out to be 1/15, 8/15 and 6/15 respectively, beginning with the third last  $B_v$ , if we take  $p$  to be one half for this purpose. A weighted  $B_v$  is calculated accordingly and multiplied into the f-'end contribution'.

For  $U$ ,  $E$  and  $B_v$  in wave numbers, the appropriate constant in front of the integral for  $f$  is  $r_e B_e^{1/2}$  and for  $g$  is  $r_e^{-1} B_e^{-1/2}$ . These constants are readily included in the program so that  $f$  and  $g$  are produced, then  $r_{1,2}$  from equation (1).

### 3. RESULTS

Turning points are shown to three decimal places at an interval of one half in  $V$  in tables 1-10 for the following molecular states:  $C_2$ ,  $X^3\Pi_u$ ,  $A^3\Pi_g$ ,  $B^3\Pi_g$ ,  $c^1\Pi_g$ ;  $O_2$ ,  $X^3\Sigma_g^-$ ,  $B^3\Sigma_u^-$ ;  $OH$ ,  $X^2\Pi_1$ ,  $A^2\Sigma^+$ ;  $SiO$ ,  $X^1\Sigma^+$ ,  $A^1\Pi$ . Potentials for the ground states of  $C_2$  and  $OH$  were previously published (Jarman 1960a) but have been extended and revised slightly. It is perhaps worth mentioning that agreement is nearly perfect to four figures between I.B.M. results for certain states not listed in this report, and those published last year on the basis of the series method.

Experimental data have been more carefully surveyed than before, reference having been made in almost every instance to original

papers named by Herzberg (1950) and papers published since 1950. The source of the data is given with each table.

Table 6 deserves special comment since turning points have been calculated to the level  $v = 21$ , which is within possibly  $12-13 \text{ cm}^{-1}$  of the convergence limit (Brix and Herzberg 1954).  $r$ -values on the repulsive side of the curve reach a minimum of  $1.330\text{\AA}$  at about  $V = 17.5$ , then show an unreal increasing trend, varying irregularly from  $1.331$  to  $1.338$ . Such behaviour is likely due to high sensitivity of  $f$  and  $g$  to small errors in the experimental data in that region, because these produce large changes in the function  $S$  (cf. Vanderslice, Mason and Maisch 1960).

#### 4. APPLICATION

The intention is to use tabulations of 'true' potential energy functions  $U(r)$ , computed in this way (but inverted by interpolation so that  $r$  is the independent variable), in the reduced Schrödinger equation

$$(5). \quad \frac{d^2\psi}{dr^2} + \frac{8\pi^2\mu}{h^2} [E - U(r)] \psi = 0$$

Methods of solving (5) for more accurate vibrational wave functions  $\psi$  by step-by-step integration processes are at present being tested.

TABLE 1

$C_2 X^3\Pi_u$

V	Energy ( $cm^{-1}$ )	$r_1(A)$	$r_2(A)$
0.5	817.8	1.257	1.374
1.0	1629.7	1.236	1.402
1.5	2435.8	1.220	1.425
2.0	3236.1	1.208	1.445
2.5	4030.4	1.197	1.463
3.0	4819.0	1.188	1.479
3.5	5601.8	1.179	1.495
4.0	6378.7	1.171	1.510
4.5	7149.9	1.164	1.525
5.0	7915.0	1.158	1.539
5.5	8674.3	1.152	1.553
6.0	9427.9	1.146	1.566
6.5	10176	1.140	1.579
7.0	10918	1.135	1.592
7.5	11654	1.130	1.605
8.0	12384	1.126	1.618
8.5	13108	1.121	1.630
9.0	13827	1.117	1.642
9.5	14540	1.113	1.655
10.0	15247	1.109	1.667
10.5	15948	1.105	1.678
11.0	16643	1.102	1.690
11.5	17332	1.098	1.702
12.0	18016	1.095	1.714
12.5	18693	1.091	1.726

Phillips (1948)

TABLE 2

$C_2 A^3 N_g$

V	Energy ( $cm^{-1}$ )	$r_1(A)$	$r_2(A)$
0.5	889.9	1.213	1.325
1.0	1771.5	1.193	1.352
1.5	2643.6	1.178	1.375
2.0	3506.5	1.166	1.394
2.5	4360.0	1.156	1.412
3.0	5203.2	1.147	1.429
3.5	6035.6	1.139	1.445
4.0	6857.2	1.132	1.461
4.5	7667.9	1.126	1.476
5.0	8469.3	1.120	1.492
5.5	9253.6	1.114	1.507
6.0	10021	1.109	1.523
6.5	10771	1.104	1.539
7.0	11507	1.100	1.554
7.5	12227	1.096	1.570
8.0	12929	1.092	1.587
8.5	13614	1.088	1.603
9.0	14277	1.084	1.620
9.5	14919	1.081	1.638
10.0	15539	1.077	1.657
10.5	16138	1.074	1.676

Phillips (1948)

TABLE 3

$C_2 B^3\Pi_g$

$v$	Energy ( $cm^{-1}$ )	$r_1(A)$	$r_2(A)$
0.5	543.8	1.470	1.614
1.0	1070.6	1.445	1.652
1.5	1580.4	1.427	1.685
2.0	2075.9	1.413	1.714
2.5	2559.9	1.401	1.741
3.0	3032.4	1.391	1.766
3.5	3493.3	1.382	1.791
4.0	3945.0	1.373	1.815
4.5	4388.2	1.366	1.838
5.0	4822.9	1.359	1.861
5.5	5249.0	1.352	1.884

Phillips (1949)

TABLE 4

$C_2 \ c^1\Pi_g$

V	Energy ( $cm^{-1}$ )	$r_1$ (A)	$r_2$ (A)
0.5	900.1	1.203	1.315
1.0	1790.8	1.183	1.342
1.5	2664.5	1.169	1.365
2.0	3521.3	1.157	1.386
2.5	4361.1	1.147	1.405
3.0	5180.4	1.139	1.425
3.5	5965.7	1.131	1.445
4.0	6716.9	1.125	1.466
4.5	7433.9	1.119	1.488
5.0	8096.2	1.114	1.515
5.5	8693.0	1.110	1.545
6.0	9224.1	1.106	1.580
6.5	9689.7	1.102	1.620

Herzberg and Sutton (1940)



TABLE 5  
O<sub>2</sub> X<sup>3</sup>Σ<sub>g</sub><sup>-</sup>

V	Energy (cm <sup>-1</sup> )	r <sub>1</sub> (Å)	r <sub>2</sub> (Å)
0.5	787.2	1.159	1.262
1.0	1568.4	1.140	1.287
1.5	2343.6	1.127	1.308
2.0	3112.8	1.116	1.325
2.5	3876.2	1.106	1.341
3.0	4633.8	1.098	1.356
3.5	5385.5	1.091	1.370
4.0	6131.4	1.084	1.384
4.5	6871.5	1.078	1.397
5.0	7605.9	1.072	1.410
5.5	8334.6	1.067	1.422
6.0	9057.5	1.062	1.434
6.5	9774.7	1.057	1.446
7.0	10486	1.053	1.457
7.5	11192	1.049	1.469
8.0	11892	1.045	1.480
8.5	12587	1.041	1.491
9.0	13276	1.037	1.502
9.5	13959	1.034	1.513
10.0	14637	1.031	1.524
10.5	15309	1.027	1.534
11.0	15975	1.024	1.545
11.5	16636	1.021	1.556
12.0	17290	1.018	1.566
12.5	17940	1.016	1.577
13.0	18583	1.013	1.587
13.5	19221	1.011	1.598
14.0	19854	1.008	1.608
14.5	20480	1.005	1.619
15.0	21101	1.003	1.629
15.5	21716	1.001	1.640

Feast (1950)  
Herzberg (1950)

TABLE 6

 $O_2 \ B^3\Sigma_u^-$ 

V	Energy ( $cm^{-1}$ )	$r_1$ (Å)	$r_2$ (Å)
0.5	343.1	1.531	1.688
1.0	686.8	1.505	1.727
1.5	1031.1	1.487	1.758
2.0	1366.7	1.471	1.788
2.5	1696.3	1.458	1.815
3.0	2020.0	1.446	1.840
3.5	2337.7	1.436	1.865
4.0	2649.7	1.427	1.889
4.5	2955.3	1.419	1.912
5.0	3254.4	1.411	1.936
5.5	3547.1	1.405	1.960
6.0	3831.1	1.398	1.985
6.5	4108.3	1.392	2.008
7.0	4378.7	1.386	2.032
7.5	4642.3	1.380	2.056
8.0	4897.9	1.376	2.083
8.5	5144.4	1.373	2.111
9.0	5381.7	1.369	2.139
9.5	5609.9	1.365	2.168
10.0	5829.4	1.360	2.196
10.5	6038.8	1.355	2.226
11.0	6238.0	1.351	2.259
11.5	6427.0	1.349	2.296
12.0	6603.8	1.346	2.336
12.5	6770.1	1.344	2.377
13.0	6925.8	1.341	2.420
13.5	7071.0	1.339	2.467
14.0	7204.1	1.337	2.520
14.5	7326.0	1.336	2.577
15.0	7436.6	1.334	2.639
15.5	7536.0	1.333	2.709
16.0	7625.0	1.332	2.783
16.5	7705.0	1.331	2.864
17.0	7776.0	1.331	2.954
17.5	7837.9	1.330	3.057
18.0	7892.3		3.165
18.5	7940.0		3.285
19.0	7981.2		3.420
19.5	8015.7	Average	3.576
20.0	8044.6	1.335	3.750
20.5	8068.3		3.957
21.0	8086.9		4.217
21.5	8100.3		4.574

Lochte-Holtgreven and Dieke (1929)

Curry and Herzberg (1934)

Knauss and Ballard (1935)

Brix and Herzberg (1954)

TABLE 7  
OH  $\chi^2 \Pi_1$

V	Energy ( $\text{cm}^{-1}$ )	$r_1(\text{\AA})$	$r_2(\text{\AA})$
0.5	1848.5	0.883	1.080
1.0	3654.5	0.852	1.134
1.5	5418.1	0.831	1.179
2.0	7140.6	0.814	1.219
2.5	8822.1	0.799	1.257
3.0	10463	0.787	1.294
3.5	12062	0.776	1.330
4.0	13621	0.767	1.365
4.5	15140	0.758	1.399
5.0	16618	0.751	1.434
5.5	18055	0.744	1.469
6.0	19451	0.737	1.503
6.5	20807	0.731	1.538
7.0	22121	0.726	1.573
7.5	23395	0.720	1.609
8.0	24623	0.715	1.646
8.5	25807	0.711	1.684
9.0	26947	0.707	1.724
9.5	28042	0.703	1.764

Herman and Hornbeck (1953)

Chamberlain and Roesler (1955)

Wallace (1960)

TABLE 8

OH  $A^2\Sigma^+$

V	Energy ( $\text{cm}^{-1}$ )	$r_1$ (A)	$r_2$ (A)
0.5	1566.5	0.918	1.133
1.0	3084.8	0.886	1.193
1.5	4555.1	0.863	1.244
2.0	5976.5	0.846	1.292
2.5	7348.0	0.832	1.338
3.0	8669.6	0.819	1.383
3.5	9941.3	0.809	1.427
4.0	11162	0.800	1.471
4.5	12331	0.791	1.516
5.0	13448	0.784	1.562
5.5	14514	0.777	1.609

Dieke and Crosswhite (1948)

TABLE 9

SiO X<sup>1</sup>Σ<sup>+</sup>

V	Energy (cm <sup>-1</sup> )	r <sub>1</sub> (Å)	r <sub>2</sub> (Å)
0.5	619.2	1.460	1.563
1.0	1235.5	1.441	1.588
1.5	1848.8	1.427	1.607
2.0	2459.2	1.416	1.624
2.5	3066.6	1.406	1.639
3.0	3671.0	1.397	1.653
3.5	4272.5	1.389	1.666
4.0	4871.0	1.382	1.679
4.5	5466.6	1.375	1.691
5.0	6059.2	1.369	1.703
5.5	6648.8	1.364	1.714
6.0	7235.5	1.358	1.725
6.5	7819.2	1.353	1.736
7.0	8400.0	1.348	1.746
7.5	8977.8	1.344	1.756
8.0	9552.6	1.339	1.766
8.5	10125	1.335	1.776

Lagerqvist and Uhler (1953)

TABLE 10

SiO A<sup>1</sup><sub>Π</sub>

V	Energy (cm <sup>-1</sup> )	r <sub>1</sub> (Å)	r <sub>2</sub> (Å)
0.5	424.7	1.562	1.687
1.0	846.3	1.540	1.717
1.5	1264.6	1.524	1.742
2.0	1679.7	1.511	1.763
2.5	2091.5	1.500	1.783
3.0	2500.2	1.490	1.801
3.5	2905.6	1.481	1.819

Lagerqvist and Uhler (1953)

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